POLYURETHANE MATERIAL FOR TWO AND THREE PIECE GOLF BALLS AND METHOD

CROSS-REFERENCE TO RELATED APPLICATIONS

A claim of benefit is made to U.S. Application Serial Nos. 09/018,283, filed February 4, 1998, and 09/030,332, filed February 25, 1998, abandoned, the contents of which are incorporated herein by reference. This is a continuation-in-part application of a regular utility application filed February 25, 1998 which is a continuation-in-part application of a regular utility application filed February 4, 1998, the contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

This invention relates to novel chemical compositions for golf ball covers that provide improved manufacturability and playability characteristics.

2. DESCRIPTION OF THE RELATED ART

Until the late 1960's, most golf balls were constructed with a thread wound core and a cover of compounds based on natural (balata and gutta percha) or synthetic transpolyisoprene. These golf balls have been and are still known to provide good flight distance. Additionally, due to the relative softness of the balata cover, skilled golfers can impart various spins on the ball in order to control the ball's flight path (e.g., "fade" or "draw") and "bite" characteristics upon landing on a green.

"Fade" is the term used in golf to describe a particular golf ball flight path that is characterized by a curved or arched flight exhibited towards the latter portion of the flight path that veers off from the center line of the initial flight path to the right of a right-handed golfer. Upon contact with the ground, a ball hit with "fade" will stop in a relatively short distance. "Fade" results from imparting clockwise sidespin on the golf ball.

"Draw" is the term used in golf to describe a particular golf ball flight path that is characterized by a curved or arched flight exhibited towards the latter portion of the flight path that veers off from the center line of the initial flight path to the left of a right-handed golfer. Upon contact with the ground, a ball hit with "draw", unlike a ball hit with "fade", will roll for a considerable distance until coming to rest. "Draw" results from imparting counter-clockwise sidespin on the golf ball.

"Bite" is the term used in golf to describe the effect of imparting a substantial amount of backspin to an approach shot to a green which causes the golf ball to stop abruptly upon contact with the green.

Another desirable feature of balata-based compounds is that they are readily adaptable to molding. These compounds therefor can be easily compression molded about a spherical core to produce golf balls.

Though possessing many desirable properties, there are substantial drawbacks to use of balata or transpolyisoprene-based

compounds for golf ball covers. From a manufacturing standpoint, balata-type materials are expensive and the manufacturing procedures used are time consuming and labor-intensive, thereby adding to the material expense. From a player's perspective, golf balls constructed with balata-based covers are very susceptible to being cut from mishits and being sheared from "sharp" grooves on a club face. As a result, they have a relatively short life span.

In response to these drawbacks to balata-based golf ball covers, the golf ball manufacturing industry has shifted to the use of synthetic thermoplastic materials, most notably ionomers sold by E. I. DuPont De Nemours & Company under the name SURLYN.

Thread wound balls with ionomer covers are less costly to manufacture than balls with balata covers. They are more durable and produce satisfactory flight distance. However, these materials are relatively hard compared to balata and thus lack the "click" and "feel" of a balata covered golf ball. "Click" is the sound emitted from the impact of a golf club head on a golf ball. "Feel" is the overall sensation transmitted to the golfer through the golf club after striking a golf ball.

In an attempt to overcome the negative factors of the hard ionomer covers, DuPont introduced low modulus SURLYN ionomers in the early 1980's. These SURLYN ionomers have a flexural modulus of from about 3000 to about 7000 PSI and hardness of from 25 to about 40 as measured on the Shore D scale - ASTM 2240. The low modulus ionomers are terpolymers, typically of ethylene,

methacrylic acid and n- or iso-butylacrylate, neutralized with sodium, zinc, magnesium or lithium cations. E.I. DuPont De Nemours & Company has disclosed that the low modulus ionomers can be blended with other grades of previously commercialized ionomers of high flexural modulus from about 30,000 to 55,000 PSI to produce balata-like properties. However, "soft" blends, typically 52 Shore D and lower (balata-like hardness), are still prone to cut and shear damage.

The low modulus ionomers when used without blends, produce covers with very similar physical properties to those of balata, including poor cut and shear resistance. Worse, wound balls with these covers tend to go "out-of-round" quicker than wound balls with balata covers. Blending with hard SURLYN ionomers was found to improve these properties.

Another approach taken to provide a golf ball cover that has the playing characteristics of balata is described in U.S. Patent No. 5,334,673 ("the `673 patent") assigned to the Acushnet Company. The '673 patent discloses a cover composition comprising a diisocyanate, a polyol and a slow-reacting polyamine curing agent. The diisocyanates claimed in the '673 patent are relatively fast reacting. Due to this fact, catalysts are not needed to lower the activation energy threshold. However, since relatively fast-reacting prepolymer systems are used, the reaction rate cannot be easily controlled thereby requiring the implementation of substantial processing controls and precise reactant concentrations in order to obtain a desired product.

To avoid the problems associated with fast-reacting prepolymer systems, slow-reacting systems such as Toluene diisocyanate (TDI) prepolymer systems can be employed. However, these systems, while avoiding the problems associated with fast-reacting systems, present similar problems, albeit for different reasons. The most noteworthy problem with slow-reacting prepolymer systems is the requirement for a catalyst.

By introducing a catalyst into the system, processing problems similar to those associated with fast-reacting prepolymer systems are virtually inevitable. As is well known in the art, the use of a catalyst can severely restrict the ability to control the speed of the reaction, which is undesirable.

It has now been discovered that a blend of diamine curing agents with slow-reacting prepolymer systems eliminates the problems associated with catalysts while maintaining the advantages associated with slow-reacting prepolymer systems. Accordingly, it is an object of the present invention to provide a golf ball cover composition that does not require a catalyst.

It is another object of the present invention to provide a golf ball having a synthetic cover material that achieves the click, feel, playability and flight performance qualities of balata covered golf balls.

It is yet another object of the invention to provide a polyurethane formula that achieves hardness characteristics similar to those associated with balata without compromising the durability of the polyurethane material. In contrast,

polyurethane systems such as those disclosed in the `673 patent produce relatively high hardness ranges that obviate the possibility of providing a polyurethane system that can truly mimic the feel and playability of a balata-based product.

A further object of the present invention is to provide a golf ball cover material that has improved process manufacturing as well as improved durability and resilience over balata.

SUMMARY OF THE INVENTION

Polyurethane compositions comprising the reaction of a polyurethane prepolymer and a curing agent are disclosed. The prepolymer comprises a diisocyanate such as Toluene diisocyanate (TDI) and a polyol such as polytetramethylene ether glycol (PTMEG). The curing agent is a blend of a slow-reacting diamine with a fast-reacting diamine such as dimethylthio 2,4-toluenediamine and diethyl 2,4-toluenediamine, respectively.

In a preferred embodiment, TDI prepolymer having a low free isocyanate content (low free TDI) is used to reduce adverse effects that can arise from exposure to unreacted isocyanate. The curing agent blend provides flexibility to the formulation by eliminating the need for a catalyst.

The present invention provides a composition suitable for molding a durable golf ball cover with the desirable characteristics of a balata golf ball cover.

These and other objects and features of the present invention will be apparent from a reading of the following

detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a Differential Scanning Calorimeter ("DSC") graph of one embodiment of the polyurethane system of the present invention using a "low temperature" golf ball cure, as desired.

FIG. 2 is a DSC graph of the same embodiment as FIG. 1 using an extended "high temperature" golf ball cure.

FIG. 3 is a schematic of a first step of the molding process according to one embodiment of the invention.

FIG. 3a is a top view of a first mold half according to one embodiment of the invention.

FIG. 3b is a side view of a first mold half according to one embodiment of the invention.

FIG. 3c is a top view of a second mold half according to one embodiment of the invention.

FIG. 3d is a side view of a second mold half according to one embodiment of the invention.

FIG. 3e is a side view of a wedge according to one embodiment of the invention.

FIG. 3f is a plan view of the golf ball molding apparatus.

FIG. 3g is a side elevational view of an x-y table, mold half and mix head according to one embodiment of the invention.

FIG. 3h is a top view of an x-y table in relation to a conveyor belt of the golf ball molding apparatus.

FIG. 3i is a front elevational view of a mold holding

apparatus, mold half and conveyor belt of the golf ball molding apparatus according to one embodiment of the invention.

FIG. 3J is a side elevational view of a core holding apparatus and core rack in relation to a conveyor belt holding a pair of mold halves according to one embodiment of the invention.

FIG. 3k is a side elevational view of a core holding apparatus holding a core over a mold half according to one embodiment of the invention.

FIG. 3l is a bottom view of a core holding apparatus according to one embodiment of the invention.

FIG. 3m is an end view of a cooling booth according to one embodiment of the invention.

FIG. 3n is an elevational view of a core spraying apparatus according to one embodiment of the invention.

FIG. 4 is a schematic of one step of the molding process according to one embodiment of the invention.

FIG. 5 is a schematic of another step of the molding process according to one embodiment of the invention.

FIG. 6 is a schematic of a further step of the molding process according to one embodiment of the invention.

FIG. 7 is a schematic of a still further step of the molding process according to one embodiment of the invention.

FIG. 8 is a schematic of yet another step of the molding process according to one embodiment of the invention.

FIG. 9 is a schematic of a yet further step of the molding process according to one embodiment of the invention.

FIG. 10 is a still another step of the molding process according to one embodiment of the present invention.

FIG. 11 is a golf ball according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

As is well known in the art, polyurethane can result from a reaction between an isocyanate-terminated polyurethane prepolymer and a curing agent. As shown in FIG. 3, the polyurethane prepolymer is produced when a diisocyanate is reacted with a polyol. The prepolymer is then reacted with the curing agent. The curing agent can be either a diamine or a polyol. Production of the prepolymer before addition to the curing agent is known as the prepolymer process. In what is known as a one-shot process, the three reactants, diisocyanate, polyol and curing agent are combined in one step. Of the two processes, the prepolymer process is preferred since it allows for greater control over the reaction. Nevertheless, the present invention can be produced using either process.

In one embodiment as shown in FIGS. 3-10, the prepolymer comprised of diisocyanate and polyol is heated to approximately 140°F while the curing agent is heated to approximately 72°F. The two materials are then mixed in the mixer, along with a colorant, and poured into a first set of golf ball mold halves and allowed to react for approximately 55 to 60 seconds. Within

this time, a golf ball core is suspended in the mold halves until the polyurethane has partially cured. A second set of mold halves is then filled with the same polyurethane mixture. The first set of mold halves are then inverted and placed over the second mold halves so that a complete ball is produced. The specifics of the process are explained in greater detail below.

Of notable importance to the present invention is the variety of curing agents that have been previously used to produce urethane elastomers. For example, the curing agents disclosed in the `673 patent are slow-reacting polyamines or polyols. As described in the `673 patent, slow-reacting polyamines are diamines that have amine groups which are sterically and/or electronically hindered by electron withdrawing groups or bulky groups situated proximate to the amine reaction sites. The spacing of the amine reaction sites will also affect the reactivity speed of the polyamines.

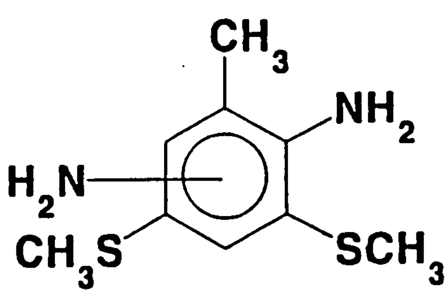
When slow-reacting polyamines are used as the curing agent to produce urethane elastomers, a catalyst is typically needed to promote the reaction between the urethane prepolymer and the curing agent. Unfortunately, as is well known in the art, the use of a catalyst can have a significant effect on the ability to control the reaction and thus, on the overall processibility.

To eliminate the need for a catalyst, a fast-reacting curing agent can be used. Such fast-reacting curing agents, e.g., diethyl-2,4-toluene diamine, do not have electron withdrawing groups or bulky groups that interfere with the reaction groups.

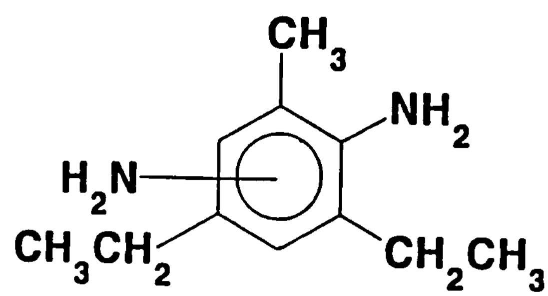
However, the problem with lack of control associated with the use of catalysts is not completely eliminated since fast-reacting curing agents are also relatively difficult to control.

It has now been discovered that a blend of a slow-reacting curing agent and a fast-reacting curing agent eliminates the problems associated with using either type of curing agent in isolation. The ultimate result of such a combination is the realization of greater control and concomitant flexibility over the reactions used to produce urethane elastomers.

In accordance with the present invention, the curing agents used are substantially as shown below:



Ethacure® 300



Ethacure® 100

One advantage that warrants immediate mention is the elimination of a post cure period. One of the major drawbacks with prior systems is the requirement for a post cure period during which other components of a golf ball can be detrimentally affected by the curing process. For example, it is not unusual for golf balls made with known polyurethane systems to require a

post cure at temperatures exceeding 140°F for over eight hours. Three-piece golf balls with rubber windings exhibit reduced compression when exposed to such "high temperature" post cure conditions. Specifically, when rubber windings are used in three-piece golf balls, long exposure to high heat leads to relaxation of the windings or thread and hence reduction in compression values and initial velocity. With the curing agent blend of the present invention, the problems associated with a post cure period are effectively eliminated.

With respect to the diisocyanate component, it is well known in the golf ball industry that toluene diisocyanate (TDI) provides additional processing flexibility to the system unlike any other diisocyanate tested. For example, when 4,4'-diphenylmethane diisocyanate (MDI) is used, the ratio tolerances (prepolymer-to-curing-agent ratio) are much less flexible compared to when TDI is used. Unless strict ratios are adhered to, urethane polymers made with MDI will not have the desired end properties, such as hardness and compression.

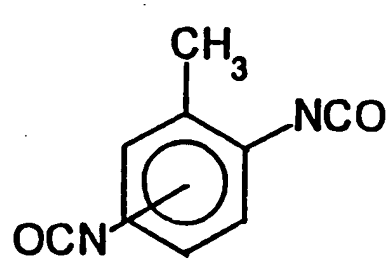
A still further problem with MDI is that it reacts much faster when reacted with an amine curing agent than does TDI. Thus, some of the control achieved by using the aforementioned curing agent blend is lost when MDI is used.

An additional disadvantage with an MDI-based system is the need for an elevated curing temperature even though a post-cure period is eliminated by the curing agent blend. Although MDI-based systems can be cured at room temperature by using curing

agents such as Polamine® (Polaroid Corporation), the system is cost prohibitive. Polamine® costs as much as four times the equivalent amount of the curing agents used in the present invention. This renders the use of Polamine® much less cost effective.

In contrast, a TDI-based system is essentially a low-cost "room temperature cure system" in that once the TDI-based polyurethane prepolymer is reacted with the curing agent blend, the composition can be cured at room temperature. This prevents any adverse effects an elevated curing temperature could have on the threading and/or core of the golf ball being produced.

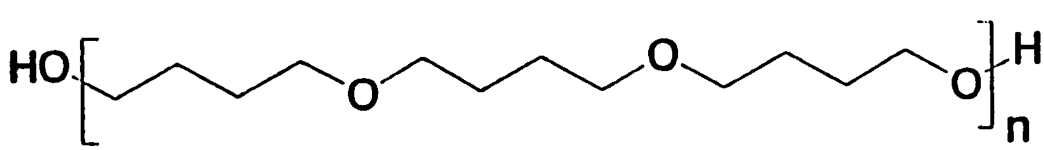
Accordingly, in order to maximize the reaction control obtained by using the curing agent blend, TDI has proven to be the best choice for the diisocyanate component. A TDI-based polyurethane system not only complements but enhances the slow reacting system achieved using the curing agent blend. The diisocyanate used in accordance with the present invention is substantially the diisocyante shown below:



TDI

A similar situation was discovered when selecting the polyol component. For the slow curing system of the present invention, the preferred polyol is polytetramethylene ether glycol (PTMEG). Like urethane elastomers made with other ether polyols, urethane elastomers made with PTMEG exhibit good hydrolytic stability and good tensile strength. Hydrolytic stability allows for a golf ball product that is substantially impervious to the effects of moisture. Thus, a golf ball made with a polyurethane system that has an ether glycol for the polyol component will have a longer shelf life, i.e., retains physical properties under prolonged humid conditions.

Unlike urethane elastomers made with other ether polyols, e.g., polypropylene ether glycol, urethane elastomers made with PTMEG exhibit superior dynamic properties such as coefficient of restitution (COR) and Bashore rebound. The polyurethane-polyurea chemical links that are formed, when PTMEG is used with a diamine curing agent, provide good thermal stability under elevated temperatures. As a result, hardness stability can be achieved. The polyol used in accordance with the present invention is substantially as shown below:



PTMEG (n= 4 to 6)

The polyurethane compositions of the invention are prepared by reacting a prepolymer of a diisocyanate and a polyol. The prepolymer must have an NCO% content of between 5.5% and 8.0% by weight of the prepolymer. Preferably the NCO% content is about 6% by weight.

In one embodiment, 100 grams of a prepolymer (6% NCO) comprising low free TDI and PTMEG is combined with 13.2 grams of a curative being a 50/50 blend of Ethacure® 300 and Ethacure® 100 (utilizing a stoichiometry of 95%). The prepolymer is heated to 140°F in a vat **1** as shown in FIG. 3. The prepolymer and curative components are combined and mixed together in a mixer **3** as shown in FIG. 3. The mixture **5** is poured via mix head **41** into a cavity **40** of a first mold half **4** that is preheated to approximately 160°F in an oven **72** as shown in FIGS. 3f,3g and 4. The gel time or pot life for this mixture is approximately 55 - 70 seconds.

In a preferred embodiment, mold half **4** is releasably joined with second mold half **7** via mated keyhole slots and pins. As shown in FIGS. 3a and 3b, pins **30** extend laterally from a side of mold half **4** and engage keyhole slots **33** provided in second mold half **7** (FIGS. 3c and 3d). Transportation of mold halves **4** and **7** is accomplished by a conveyor **47** as shown generally in FIG. 3f. To begin the process, mold halves **4** and **7** are preheated in oven **72**. After heating, the mated mold halves are transported to a

cover material loading station **A**. A mold removal cylinder **45a** pushes the joined mold halves off conveyor **47** and onto a table **42** known as an X-Y table. The two mold halves are filled with mixture **5** sequentially via positioning under mix head **41** extending from mixer **3**. Positioning of the mold halves under the stationary mix head **41** is accomplished by moving table **42** upon which the mold halves have been placed. The computer-guided X-Y table **42** is selectively moved under mix head **41** after the mold halves have been mechanically placed on a preselected initial spot on the X-Y table which is bounded by an angular x-y table stop **45** as shown in FIGS. 3g and 3h. After the mold halves have been placed, table **42** is moved along two axes on two pairs of perpendicular rails, first x-y table rails **43** and second x-y table rails **44**, in order to center each mold cavity **40** under mix head **41**. Once the mold cavities **40** are filled, the mated mold halves are mechanically pushed onto a conveyor belt **47** by mold return cylinder **45b** so that the mold halves can be transported to a core loading station **B**.

Referring to FIGS. 3f,3j and 3k, initial alignment of the mold cavities with a core loading apparatus **48** along three axes is accomplished by the combination of conveyor belt **47**, guide rails **49** situated above each lateral edge of conveyor belt **47** and

a core loading station end stop **50** extending inwardly over conveyor belt **47** from one lateral edge of a conveyor belt support frame **51**. The height of guide rails **49** and end stop **50** above conveyor belt **47** is set to physically engage the mated mold halves.

Guide rails **49** provide initial lateral alignment (x axis alignment), of the mold halves relative to the core loading apparatus **48**. It is important to the function of the system that guide rails **49** be situated such that the mated mold halves do not bind between guide rails **49**.

End stop **50** arrests movement of the mated mold halves on the constantly moving conveyor belt **47** and provides initial alignment of the mold halves with the core loading apparatus **48** along a y axis which runs along the length of conveyor belt **47**. Conveyor belt **47** provides initial alignment of the mold halves with core loading apparatus **48** along a z or vertical axis.

Following initial alignment of the mated mold halves with core loading apparatus **48**, after approximately 35 seconds, a golf ball center or wound core **6** is lowered into a cavity **40** of mold half **4** which contains "semi-gelled" polyurethane **5** as shown in FIG. 5.

With respect to three-piece balls having wound cores, prior to placement in cavity **40**, wound core **6** is sprayed with a

polyurethane-based liquid to protect the windings from the high temperatures of mixture **5** as shown in FIG. 3n. Without the polyurethane coating, the windings would denature and lose tension when subjected to the relatively high temperatures of mixture **5**.

As shown in FIG. 3n, the core spraying station is comprised of a conveyor **80** upon which core holding assemblies **81** are attached. Core holding assemblies **81** have three pin-like fingers set approximately 120° apart to support cores **6**. A polyurethane spray head **82** envelopes cores **6** with a polyurethane liquid **83** that dries at ambient temperatures.

Turning back to the golf ball molding apparatus and referring again to FIGS. 3j and 3k, placement of core **6** into polyurethane gel-filled cavity **40** is accomplished with a vacuum pickup **52** that uses vacuum pressure to "grasp" and "hold" core **6**. Vacuum pickup **52** is attached to core holding apparatus **48** which is suspended by two parallel pairs of perpendicularly oriented guide rails, first core holding apparatus rails **52b** and second core holding apparatus rails **52c**, which allow for the movement of core holding apparatus **48** along two axes. Once a core **6** has been secured to vacuum pickup **52** from a core holding channel **52a**, core holding apparatus **48** is moved, via computer guidance, into position over cavity **40** so that vacuum pickup **52** is situated over

the exact hemispherical center of cavity **40**. As shown in FIG. 31, vacuum pickup **52** has apertures **53** which contain bushings **54** which are sized to matingly engage vertical pins **37** which project upwardly from mold half **4**. The mating of vertical pins **37** and apertures **53**/bushings **54** provide a second final alignment. Vacuum pickup **52** is then lowered so that the center or core **6** (depending on whether the golf ball being manufactured is a two-piece or three-piece ball, respectively), is partially engulfed by the "semi-gelled" polyurethane **5** and positioned to be in the exact center of the finished golf ball.

As stated, final alignment occurs when pins **37** are mated with apertures **53**/bushings **54**. It is important to note that the combination of the pins and apertures do not alone hold mold half **4** in place. At all times, pins **37** are free within apertures **53**. Any movement restriction of mold half **4** is accomplished by the combination of apertures **53** of the core holding apparatus **48**, pins **37** and conveyor belt **47** which exerts a force on, and supports, mold half **4**.

As described above, shortly after the first mold half **4** is filled with the polyurethane mixture **5** (about between 12-20 seconds later), a second mold half **7** is filled with the same polyurethane mixture **5** as shown in FIG. 7. After approximately

20 - 30 seconds of core hold time in mold half **4**, first mold half **4** is mated with second mold half **7** containing the same polyurethane prepolymer-diamine curing agent mixture by inverting the first mold half **4** as shown in FIGS. 8 and 9.

Referring now to FIG. 3i, a mold holding apparatus **55** configured in the shape of a two tine fork as shown in FIG. 3i, has tines **56** which are spaced to accommodate the length dimension of the mold halves. Mold holding apparatus **55** is independent from core holding apparatus **48** and is suspended from a frame that is attached to two parallel pairs of rails, first mold holding apparatus rails **57** and second mold holding apparatus rails **58**, which are oriented perpendicularly to allow movement of the mold holder in two axes. Tines **56** of mold holding apparatus **55** have rotatable mold grippers **59** situated at distal ends of tines such that mold grippers **59** face inwardly. Mold grippers **59** are designed to releasably attach to the mold halves.

Shortly after core holding apparatus **48** releases core **6**, preferably within a fraction of a second later, mold holding apparatus **55** is lowered to allow engagement of mold grippers **59** with mold half **4**. After engagement, mold holding apparatus **55** is raised thereby detaching first mold half **4** from second mold half **7**. At this time, second mold half **7** is still stationary as its movement is arrested by end stop **50**.

After mold half **4** has been lifted a predetermined height, mold grippers **59** are rotated approximately 180° so that core **6** is suspended above conveyor belt **47**. Mold holding apparatus **55** is then moved along perpendicular rails **57** and **58** until mold half **4** is situated over second mold half **7**. Mold holding apparatus **55** is then lowered until pins **37** of first mold half **4** are matingly engaged by apertures **60** in second mold half **7**. The initial alignment of mold half **4** to second mold half **7** by mold holding apparatus **55** is followed by final alignment of the mold halves when pins **37** are mated with apertures **60**. Thus, pins **37** have dual functions: 1) final alignment of core **6** with cavity **40** and, 2) final alignment of the mold halves.

Referring to FIGS. 3c and 3d, to secure the mold halves together, lateral apertures **34** which open on opposite ends of second mold half **7** are situated to be perpendicular to, and intersect, apertures **60**. Fitted loosely within lateral apertures **34** are wedges **35** (FIGS. 3d and 3e), that are sized to slidably engage the walls of lateral apertures **34**. Lateral apertures **34** open on the edges of second mold half **7** that face the lateral edges of conveyor **47** to allow for manipulation of wedges **35**.

As shown in FIG. 3b, pins **37** have slots **38** provided therein which align with lateral apertures **34** when pins **37** are matingly

engaged to apertures **60**. After first mold half **4** is placed into contact with second mold half **7**, a pancake cylinder **61** applies pressure onto a bottom surface of mold half **4** to secure mold half **4** to second mold half **7** (FIG. 3i). Simultaneously with the action of pancake cylinder **61**, wedge drivers **62** situated above a lateral edge of conveyor **47**, intermittently strike wedges **35** into slots **38** until the mold halves are securely locked together.

After approximately four minutes of heating and three minutes of cooling, the golf ball is removed from the mold and allowed to post cure at room temperature for 8-16 hours, FIGS. 9 and 10. Referring to FIG. 3f, to heat the formed golf balls, the joined mold halves are rotated onto an edge via rotation ramp **64** which causes rotation of the joined mold halves when conveyor **47** transports the mold halves into ramp **64**. The mold halves which are now oriented with the bottoms of the mold halves facing the lateral edges of conveyor **47** are transported on conveyor **47** to a heating station **C** where the golf balls are heated for approximately four minutes in a heating oven **63**. To cool the joined mold halves, the mold halves are transported to a cooling station **D** where the joined mold halves are transported through a cooling hood **65** which contains spray nozzles **66** which forcibly deliver cool water **67** to the bottoms of mold halves **4** and **7** as shown in FIG 3m.

Referring again to FIG. 3f, to disengage the joined mold halves, the mold halves are transported to a mold disengagement station **E**. A counter-rotation ramp **68a** rotates the joined mold halves onto the bottom of first mold half **4**. To arrest movement of the joined mold halves at station **E**, one of the lateral pins **37** collides with disengagement stop **68**. Slots **39** provided in opposing ends of mold half **4** are engaged by a mold holding fork **70** with tines sized to engage slots **39**. After mold half **4** has been secured by mold holding fork **70**, mold releasing pins **71** are forcibly inserted into lateral apertures **34** of second mold half **7** so that wedges **35** are moved out of engagement with pins **37**. After disengagement of wedges **35**, releasing pins **71**, while still in lateral apertures **34**, are rotated about an axis parallel to pins **71** to remove second mold half **7** from mold half **4**. Second mold half **7** is rotated 180° onto its bottom surface.

To prepare the mold halves for further use, a mold releasing agent that is coated on cavities **40** prior to use of the mold halves can optionally be reapplied, if needed, before transporting the mold halves back to heating oven **72** for further cycling through the golf ball molding process described above.

Removal of the finished golf ball from the mold is facilitated by the mold release agent. The mold release agent can be any substance, e.g., mineral oil, that can attenuate

adhesion of the polyurethane cover composition to the mold cavity. It is to be understood that the releasing agent forms no part of the invention and is described simply for purposes of thoroughness and clarity.

If desired, other ingredients, such as pigments, can be added to the mixture. For example, a pigment **2a** addition of .25 - 5% by weight of the total polyurethane prepolymer/curative mixture can be added via a third stream to the mixhead at the time of adding the prepolymer and the diamine curing agent to produce the desired color. In a preferred embodiment, the pigment shall consist of 65% TIO_2 and 35% carrier (typically a polyol, with or without toners) by weight. The pigment may or may not include other additives including a UV stabilizing package, optical brighteners, etc.

To produce a golf ball in accordance with the invention, in a preferred embodiment, 100 PPHR of prepolymer (low free TDI @ 6% NCO and PTMEG) is heated to 140°F in vat **1** as shown in FIG. 3. 13.2 PPHR of a curative comprising Ethacure® 100 and Ethacure® 300 at a 50:50 ratio is maintained at room temperature in second vat **2**. The contents of vat **1** and vat **2** are mixed in mixer **3** along with 2.3 PPHR pigment **2a** from a third vat as shown in FIG. 3. The mixture **5** is poured into a hemispherical cavity of first open mold half **4** which has a diameter of about 1.68". After approximately 35 seconds, a golf ball core **6** is lowered into the mold half **4** containing "semi-gelled" polyurethane **5** as shown in

FIG. 5.

As shown in FIG. 11, the golf ball core **6** preferably has a diameter of about 1.58" and is comprised of a solid core or center **6a** with a thread windings layer **6b** to make a two piece or three piece ball, respectively. The center preferably has a diameter of about 1.42" and is comprised of 100 PPHR high cis polybutadiene rubber, 20 PPHR Zinc Acrylate salt, 24.5 PPHR Barium Sulfate, 6 PPHR Zinc Oxide, 3 PPHR Zinc Stearate and 2.1 PPHR 1,1-Di-(tert-butylperoxy)-3,3,5-trimethyl cyclohexane (40% active). The thread windings layer is comprised of sulfur-cured polyisoprene rubber having a thread size of preferably 0.017" x 5/64" so that the thread layer thickness is about 0.08" and the combination of the center and thread windings has a diameter of about 1.58".

Shortly after the first open mold half **4** is filled with the polyurethane mixture **5**, a second hemispherical cavity situated in open mold half **7** is filled with the polyurethane mixture **5** as shown in FIG. 7. Second mold half **7** also has a diameter of about 1.68".

After approximately 20-30 seconds, the first mold half **4** is mated with the second mold half **7** containing the same polyurethane mixture **5** as contained in first mold half **4** by inverting the first mold half **4** as shown in FIGS. 8 and 9. The combination of the polyurethane mixture **5** in each of the mold

halves forms the golf ball cover **5a**. After approximately 4 minutes of heating and three minutes of cooling, the golf ball is removed from the mold, and allowed to post cure at room temperature for 8-16 hours, FIGS. 9 and 10.

To achieve the desired results, the reactants should be reacted to obtain a stoichiometry of between about 92 - 105% and preferably 95%. With respect to the NCO% content, any prepolymer used should have an NCO% between about 5.5 - 8.0% by weight of the prepolymer and preferably about 6% by weight. Systems using TDI, IPDI (Isophorone diisocyanate) or MDI as the diisocyanate and an ether backbone are all possible choices for the polyurethane prepolymer. The polyol selected should have a molecular weight of between about 650 - 3000 and preferably between about 850 - 2000. The larger the molecular weight, the softer, and more flexible the polyurethane becomes. In the preferred embodiment, PTMEG having a molecular weight of about 1000 is used to obtain desired Bashore rebound and flexural modulus performance characteristics.

The curative should be a blend of a slow-reacting diamine and a fast-reacting diamine. In a preferred embodiment, slow-reacting dimethylthio-2,4-toluenediamine sold under the trade name Ethacure 300 by the Albermarle Corporation and fast-reacting diethyl-2,4-toluenediamine sold under the trade name Ethacure 100 by Albermarle, are combined at a ratio of between about 40:60 - 80:20. Polyurethanes having desirable physical properties have been achieved using the following Ethacure 300/Ethacure 100 blend

ratios at the following equivalent weights, respectively: 40:60 at 95.76, 50:50 at 97.47, 60:40 at 99.24, 70:30 at 101.00 and 80:20 at 102.97.

As previously discussed, it is essential that a blend be used to eliminate the need for a catalyst. It has been discovered that the combination of Ethacure 100, which does not have the thio group, with Ethacure 300 enables the reaction to take place without the need of a catalyst while still achieving good gel times (a pot life of approximately 55-70 seconds). Due to the absence of the thio group, steric hindrance is not realized. However, Ethacure 100 used alone, acts rapidly and therefore does not provide the desired control over the reaction time. In contrast, Ethacure 300, due to steric hindrance, reacts much slower than Ethacure 100 and requires the undesired catalyst.

If a "room cure" formulation is desired, catalysts, such as Dabco 33 LV from Air Products, are not suitable since they provide exponential exothermic reactions. With few exceptions, once a catalyst is introduced into a urethane system, it is difficult, and, from a commercially practical standpoint, impossible to obtain a desired linear exothermic reaction. Without being able to control the temperature pattern of the reaction, it is difficult to obtain the desired physical properties since the physical properties are temperature sensitive. The curing agent blend of the present TDI-based system provides the desired exothermic reaction so that the

desired end-product physical properties can be achieved.

It has been found that a blend of these two curatives allows the reaction time to be controlled. By varying the blend, the speed of the reaction can be controlled to obtain the desired characteristics. With a catalyst, the speed of the reaction cannot be as easily controlled, which ultimately leads to undesired physical properties.

A further surprising advantage of the new system using the Ethacure 300/100 blend is the elimination of a post-cure without losing the benefits of a post-cure period. With many prior art systems, compression is lost if a "high temperature" post-cure period is instituted. With the system of the present invention, good compression numbers can be achieved without a "high temperature" post-cure period. Moreover, curing can be performed at room temperature, i.e., 72°F.

A still further surprising advantage of the preferred curing agent blend is the flexibility in formula concentrations the new system provides. To change the resulting characteristics, one need only change the concentrations of the reactants. For example, hardness readings ranging from 50D - 65D have been achieved by altering the molecular weight of the polyol component (PTMEG in the preferred embodiment), the NCO% content and/or the stoichiometry of the reaction. Even when the reactant concentrations are altered to achieve different hardness levels, good physical properties can be achieved within a range of alterations.

A yet further advantage, as is well known in the golf ball manufacturing industry, is that the ratio of polymer to curing agent is also more forgiving than other known systems. In contrast, for example, the system disclosed in the '673 patent requires the ratio to be more "exact" in order to produce the desired polymer.

The following examples are provided to illustrate and further explain the aspects of the invention. These examples are set forth for purposes of illustration and do not limit the scope of the invention.

EXAMPLE 1

A 6% low free TDI-PTMEG polyurethane prepolymer was heated to 140°F and mixed with a 50/50 blend of Ethacure 300 and Ethacure 100. The curing agent blend was maintained at room temperature before mixing. The exothermic reaction reached between 160°-170°F with a gel time of approximately 65 seconds. The mixture was cured at room temperature for 12 hours.

When tested for hardness using a Shore D Durometer made by Shore Instrument and Mfg. Co., Inc., the composition exhibited a Shore D hardness of 51.0 when measured using ASTM method D-2240-91, "Indentation Hardness of Rubber and Plastic by Means of a Durometer." A Bashore Rebound measurement of 51% was obtained in accordance ASTM D2632 with a Shore Resiliometer also made by Shore Instrument and Mfg. Co., Inc.

Tensile data was compiled using ASTM D412. The composition

produced an ultimate stress of 6269 psi, a Young's modulus reading of 5166 psi, a stress at 100% reading of 1909 psi and an elongation reading of 400 - 450% using ASTM D412. Elongation is a measurement of a material's elasticity up to its breaking point under a tensile load. This type of tensile data is obtained because it can be correlated to the ultimate performance characteristics of the polyurethane cover such as cut resistance and shear resistance.

The composition exhibited a flexural modulus of 16650 psi which falls within the desired range of 15,000 - 30,000 psi using ASTM method D-790. With respect to the polyurethane system embodiments of the present invention, flexural modulus increases as Shore D hardness increases.

The final physical parameters tested relate to tear data obtained in accordance with ASTM D624, Die C ("Graves Tear"). The composition produced a maximum load reading of 512 lbf./in., (the load at which the material samples began to tear). An energy to break reading of 24.8 lbf./in. and a energy to yield reading of 18.0 lbf./in. were also obtained.

The foregoing test results demonstrate that a polyurethane material having superior processibility can be achieved that exhibits "high" elongation, tensile strength and tear strength. When used as the material for a golf ball cover, these physical properties translate into a golf ball cover material that exhibits superior cut, abrasion and shear resistance versus ionomers and balata when stuck by hard objects such as the

grooved face of a metallic golf club head.

In addition to the physical parameter testing, the polyurethane mixture (low free TDI prepolymer mixed with a 50/50 blend of Ethacure 300/Ethacure 100) was subjected to two different post cure environments to determine the effects of the post cure on the physical properties of the polyurethane end product. One part of the mixture was cured at 105°F ("room cure temperature") for approximately 10 hours. The mixture was then allowed to cool down for approximately two weeks before testing for physical properties. The identical mixture was cured at 220°F ("extended cure") again for approximately 10 hours and allowed to cool down for approximately two weeks before testing for physical properties.

FIG. 1 shows the DSC results for the "room cure" trial and FIG. 2 shows the results for the "extended cure" trial. As is clear from the test results, the DSC curves were very similar, taking into account the accuracy of the testing apparatus and the testing method.

When the polyurethane products were tested for physical properties, the products exhibited similar physical properties. These results demonstrate that the polyurethane made with the curing agent blend could be cured without the need for a "high temperature" post cure period or "extended cure" period during which golf ball physical properties can be lost due to the exposure of the other golf ball components, e.g. windings and core, to high temperatures for long periods of time. By using

the curing agent blend of the invention, with the elimination of a "high temperature" post cure period, physical properties such as initial velocity and compression can be maintained while achieving "full" reaction of the polyurethane reaction components.

Examples 2-4

Additional tests were run using the same low free TDI prepolymer with altered blend ratios of Ethacure 300/Ethacure 100. In each test, the prepolymer was heated to 140°F and the curative blend was maintained at room temperature before being mixed. The tests were conducted to determine the blend effects on gel time and exothermic reaction.

When the blend ratio was set at 60:40 (E100 to E300), a gel time of 55-60 seconds was achieved. The exothermic reaction reached 145°F. A 70:30 blend ratio produced a gel time of approximately 50 seconds and an exothermic reaction that reached 156°F. Lastly, an 80:20 blend ratio produced a gel time of approximately 45 seconds and an exothermic reaction that reached 165°F. All of the polyurethane end products of these tests were determined to have physical characteristics similar to those of the polyurethane produced using the 50:50 curing agent blend ratio.

These test results conclusively demonstrate the processibility advantages of the curing agent blend and the wide range of blend ratios that can be used to produce desired

polyurethane end products. Depending on the amount of time needed to pour a particular number of golf ball molds with a single batch of the polyurethane prepolymer mix, a curing agent blend can be picked that will accommodate the speed requirements of the golf ball manufacturing process without having any appreciable effect on the physical characteristics of the end product.

As demonstrated by the preceding examples, there is a great deal of flexibility that can be built into the urethane elastomer system. The curing agent blend ratio can be modified to alter the speed of the reaction to accommodate the practitioner's needs while the diisocyanate NCO% content can be varied to achieve varying physical properties. No other golf ball specific urethane elastomer system is known by the inventors that provides such flexibility.

It will be appreciated that the instant specification and claims are set forth by way of illustration and not made without departing from the spirit and scope of the present invention. Having thus described my invention, what I claim as new and desire to secure by United States Letters Patent is: